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Production of $O(^1D)$ from photolysis of O_3

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Abstract. We have used a model accounting for absorption by vibrationally and rotationally excited ozone (O_3) to examine published measurements of the quantum yield of $O(^1D)$ and $O_2(^1\Delta_g)$ from O_3 photolysis in the Huggins band (305-325 nm). We conclude that the quantum yield of $O(^1D)$ is 0.2-0.3 for wavelengths between 312 and 320 nm at 298 K; in contrast, the JPL recommended quantum yield of $O(^1D)$ is negligible in this wavelength region. We present a compilation of our results at temperatures and wavelengths relevant to atmospheric calculations. Production of $O(^1D)$ from excited O_3 increases calculated concentrations of $O(^1D)$ by up to 40% and OH by 15% for the troposphere and lower stratosphere.

Introduction

Photolysis of ozone (O_3) produces $O(^1D)$ and $O_2(^1\Delta_g)$ with near unit efficiency at wavelengths shorter than 300 nm. Near 310 nm the quantum yield of these species falls rapidly as the photolysis energy approaches the energetic limit for their production from ground-state O_3. There is considerable controversy, however, concerning the value of the quantum yield of $O(^1D)$, Φ, at wavelengths (λ) longer than 310 nm. For 298 K, JPL recommended values [*DeMore et al.*, 1992] are <0.1 at λ>315 nm, where several measurements have yielded values exceeding 0.2 [*Brock and Watson*, 1980a; *Martin et al.*, 1974; *Trolier and Wiesenfeld*, 1988]. The experimentally observed "tail" has been attributed to (1) spin-forbidden production of $O(^1D)+O_2(^3\Sigma)$ [*Brock and Watson*, 1980a], (2) experimental artifact [*DeMore et al.*, 1992], or (3) photolysis of vibrationally excited O_3 [*Adler-Golden et al.*, 1982; *Trolier and Wiesenfeld*, 1988].

Hypothesis (1) is inconsistent with the apparent correlation in the tail region between measurements of $O_2(^1\Delta_g)$ [*Ball et al.*, 1993] and $O(^1D)$ [*Brock and Watson*, 1980a; *Martin et al.*, 1974; *Trolier and Wiesenfeld*, 1988] (see Figure 1). Hypothesis (2) is based on measurements in which Φ was found to be negligible in the tail region [*Arnold et al.*, 1977; *Moortgat et al.*, 1977; *Philen et al.*, 1977]. Measurements by *Philen et al.* appear to have been compromised by a wavelength-calibration error of 2 nm and are generally discounted [*Brock and Watson*, 1980a]. *Moortgat et al.* deconvolved their data to compensate for a photolysis source with low spectral resolution (3.5-4.0 nm), which may account for the absence of a tail in their published measurements. We have no explanation for the failure of *Arnold et al.* to observe the tail apparent in other experiments performed with similar techniques [*Martin et al.*, 1974; *Brock and Watson*, 1980a].

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The temperature dependence of Φ in the tail region provides a test of Hypothesis (3) since the population of O_3 in vibrationally excited states falls with decreasing temperature. Data for Φ in the tail region for temperatures lower than 298 K are only available from the low resolution experiment by *Moortgat et al.* [1977], measurements made by *Lin and Demore* [1973] at 233 K, and studies performed by *Kuis et al.* [1975] and *Kajimoto and Cvetanovic'* [1976] only at 313 nm. We have analyzed these data and those obtained at 298 K with a model that includes absorption by vibrationally and rotationally excited O_3. The results confirm that Φ(298 K) exceeds 0.2 in the tail region. This model can be used to predict Φ at temperatures outside of the range 233-298 K.

A model for production of $O(^1D)$ from photolysis of O_3

As in previous studies [*Adler-Golden et al.*, 1982; *Hudson*, 1980], we assumed that Φ at wavelength λ and temperature T is given by a sum over internal states, vJK, of the state-dependent quantum yield, $\Phi_{vJK}(\lambda)$, weighted by the population in each state, $g(B_{vJK}(T))$, and the vibrational-state-dependent absorption cross section, $\sigma_v(\lambda)$, i.e.,

$$\Phi(\lambda, T) = \frac{1}{\sigma(\lambda, T)} \sum_{vJK} g(B_{vJK}(T))(\sigma_v(\lambda))(\Phi_{vJK}(\lambda)), \quad (1)$$

where

$$\sigma(\lambda, T) = \sum_{vJK} g(B_{vJK}(T))(\sigma_v(\lambda)). \quad (2)$$

Here, $B_{vJK}(T) = \exp(-E_{int}/kT)$, k is the Boltzmann constant, E_{int} is the internal energy determined from spectroscopic constants given in *Herzberg* [1966], g is a rotational degeneracy factor assuming that O_3 is nearly a symmetric top molecule, and $\sigma(\lambda, T)$ is the total absorption cross section.

Although calculated Franck-Condon factors or measured values of $\sigma_v(\lambda)$ have not been reported for excited states of O_3 in the Huggins band, measurements of $\sigma(\lambda)$ have been performed as a function of temperature [*A. M. Bass and R. J. Paur*, unpublished data, 1984; *Molina and Molina*, 1986]. These measurements demonstrate weak vibrational structure corresponding to transitions into locally bound regions of the excited potential [*Simons et al.*, 1973; *Sinha et al.*, 1986]. For wavelengths between 300 and 325 nm, the absorption cross section increases with temperature between 203 and 298 K.

We derived an estimate of $\sigma_v(\lambda)$ for the first vibrationally excited state of each of the three vibrational modes by performing a nonlinear least-squares (NLS) fit of Eq. (2) to the data of *Bass and Paur* (which cover a broader range of temperatures than other measurements). Values of $\sigma_v(\lambda)$ are given in Table 1, along with the assignment of features where transitions have been identified. We assumed that σ_v does not vary with rotational state. Following *Adler-Golden et al.* [1982], we assumed that molecules with one quantum of vibration (v=1) in the asymmetric stretch have the same absorption

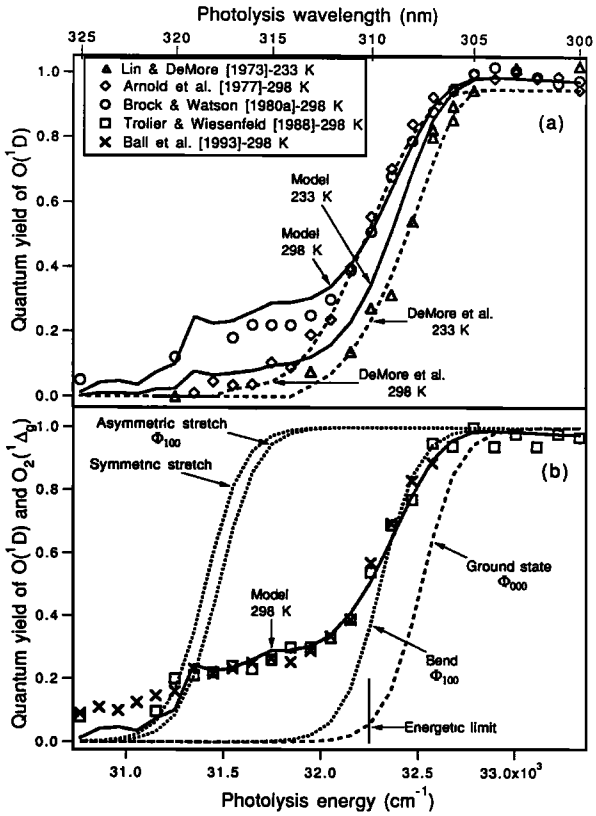

Figure 1. Model results compared with measured Φ. The solid lines are the fit to the circles and triangles for λ≤311 nm. Each data set (symbols) was normalized to give Φ(305 nm)=1, except for that of *Ball et al.* [1993], which was normalized to 0.945 at 306 nm. For clarity error bars are not included. (a) The dashed lines are the recommendations of *DeMore et al.* [1992]. (b) The dashed line is predicted for molecules with no initial internal energy. The dotted lines are predicted for the ground rotational state and the first vibrationally excited state of the asymmetric and symmetric stretches and the bend.

cross section as those with (v=1) in the symmetric stretch but allowed those with (v=1) in the bend and those in the ground state to have different cross sections.

Derived values of $\sigma_v(\lambda)$ were used in a fit to quantum yield data to determine $\Phi_{vJK}(\lambda)$. The simplest analysis would model $\Phi_{vJK}(\lambda)$ as a unit step function shifted to lower energy (longer wavelength) from the energetic threshold by an amount equivalent to the internal energy of the molecule. A molecule with sufficient internal energy, however, may not photodissociate via the $O(^1D)+O_2(^1\Delta_g)$ channel, despite its accessibility. We thus let $\Phi_{vJK}(\lambda)$ have the form of a switching function with a finite, adjustable width W_v, i.e.,

$$\Phi_{vJK}(\lambda) = \frac{1}{2}\left[1 + \mathrm{Tanh}\left(\frac{\nu - \nu_{vJK}}{W_v}\right)\right], \quad (3)$$

where ν is the photolysis energy in wavenumbers, and ν_{vJK} is a state-dependent threshold (marking the inflection point of the switching function) shifted from the threshold for molecules possessing no internal energy (ν_{000}) by an amount related to the rotational (E_{rot}) and vibrational (E_{vib}) energy associated with state vJK (see Figure 1b). Thus,

$$\nu_{vJK} = \nu_{000} - \varepsilon_{vib}E_{vib} - \varepsilon_{rot}E_{rot}, \quad (4)$$

where ε_{vib} and ε_{rot} account for the efficiency of coupling between the molecule's internal energy and the $O(^1D)+O_2(^1\Delta_g)$ photolysis channel. These parameters are less than unity if initial internal energy of the molecule is partitioned into internal or translational energy of the photolytic products. We allowed ε_{vib}, ε_{rot}, W_v, and ν_{000} to be adjustable parameters in our model.

The sensitivity of Φ to temperature is governed by these state-dependent parameters. We performed a weighted NLS fit to quantum yield data for 233 K [*Lin and Demore*, 1973] and for 298 K [*Brock and Watson*, 1980a] (normalized to unity at 305 nm to bring the 308 nm value into agreement with the absolute measurement of *Greenblatt and Wiesenfeld* [1983]). Since there is disagreement among published measurements concerning the existence of the tail, data for wavelengths longer than 311 nm were excluded from our fits; the model was used to predict values of Φ in this region.

In our fits the data for 298 K were given five times the weight of the data for 233 K to reflect our greater confidence in these measurements. The data for 298 K to which we fit our model are consistent with numerous other measurements [*Arnold et al.*, 1977; *Trolier and Wiesenfeld*, 1988; *Ball et al.* 1993], and the results are insensitive to the specific data set chosen for analysis. The data used for 233 K may have larger uncertainties (not estimated by *Lin and Demore* [1973]) than the 298 K data since the detection method used at 233 K was less direct. We did not use the data of *Moortgat et al.* [1977] because their spectral resolution (3.5-4.0 nm) was insufficient to sample the sharp feature in the fall-off region.

The NLS fit of Eq. (1) to the data gives ν_{000}=32518 cm^{-1}, $\varepsilon_{vib}(\nu_1,\nu_3)=\varepsilon_{rot}$=1, $\varepsilon_{vib}(\nu_2)$=0.300, and W_v=190 cm^{-1}. Figure 1b shows the prediction of $\Phi_{vJK}(\lambda)$ for molecules possessing no internal energy and for molecules with one quantum of energy in each of the three vibrational modes, symmetric stretch (ν_1),

Table 1. Cross sections and parameters for Eq. (5)

λ (nm)	σ_{000}	$\sigma_{v1,v3}$ (10^{-20} cm^2)	σ_{v2}	Transition	A	B (cm^{-1})
305	16.1	261	68.7		1.01	3.933
306	14.7	263	39.9		1.01	11.51
307	12.6	283	27.1		1.05	33.09
308	11.3	280	6.75		1.15	79.39
309	9.93	228	26.8		1.39	159.9
310	8.04	193	20.9		1.90	272.5
311	7.24	180	18.8		2.93	407.9
312	6.13	159	15.0		4.87	551.4
313	5.19	146	14.4		8.21	682.3
314	4.89	149	6.46		13.3	791.6
315	3.89	130	4.68		17.6	851.3
316	3.65	111	0.609		20.4	903.8
317	3.06	98.6	10.8		18.0	900.3
318	2.90	98.3	0		21.8	948.4
319	1.69	101	3.97	530 ← 100	18.1	891.1
320	2.69	65.6	0.978		17.2	1066
321	1.05	43.6	18.3	430 ← 010	7.99	969.4
322	2.04	38.1	5.04		11.5	1201
323	1.32	65.7	1.45		14.3	1182
324	0.663	59.0	2.10		10.7	1152
325	1.40	33.6	1.40		11.8	1435

bend (ν_2), and asymmetric stretch (ν_3). Only molecules with internal energy contribute to Φ beyond the energetic limit. This conclusion is supported by measurements that show that Φ increases dramatically at 314.5 nm when the asymmetric stretch is excited with an infrared laser [*Zittel and Little*, 1980].

A comparison of calculated and measured Φ is shown in Figure 1. The predicted value of Φ for λ>311 nm at 298 K reproduces the tail in the data of *Trolier and Wiesenfeld* [1988] and *Ball et al.* [1993] within experimental uncertainty. The model also agrees very well with the results of *Kuis et al.* [1975] at 313 nm over temperatures from 221 to 293 K but is systematically lower than results from a similar study by *Kajimoto and Cvetanovic'* [1976]. The temperature dependence of Φ between 305 and 311 nm results from the photolysis of molecules populating excited rovibrational states. The model, however, systematically overestimates Φ at 233 K. The discrepancy may result from: (1) uncertainties in $\sigma_v(\lambda)$, the determination of which is limited by our understanding of the spectroscopy associated with structure in the absorption spectra (e.g., shifts in the rotational distribution near vibrational resonances cause the cross section to be nonmonotonic with temperature) or (2) large uncertainties for the 233 K data.

Significant production of O(¹D) at 312-320 nm is in sharp contrast to the recommendations of *DeMore et al.* [1992] and those from J. Phys. Chem. Ref. Data [*Atkinson et al.*, 1992], which give Φ=0 for wavelengths longer than 317 nm at 298 K and 313 nm at 233 K. These recommendations are based on the data of *Arnold et al.* [1977], *Brock and Watson* [1980a], and *Trolier and Wiesenfeld* [1988] (without the tail) at 298 K and *Moortgat et al.* [1977] at lower temperatures. Results for the model of *Adler-Golden et al.* [1982] fall within the experimental uncertainty of the data of *Brock and Watson* [1980a] in the tail region. This model may have been discounted previously since it relies on analysis of data in the tail region, which had been suspected of resulting from an experimental artifact [*DeMore et al.*, 1992].

To facilitate use of our results in atmospheric calculations, we parameterized output from the full model in the range 305-325 nm according to the form

$$\Phi(\lambda, T) = A(\lambda)\exp\left[\frac{-B(\lambda)}{kT}\right]. \quad (5)$$

Results, given in Table 1, reproduce full model predictions to within 10% for temperatures in the range 185-320 K.

Figure 2 shows Φ for the spectral range 222-325 nm. All data are for 298 K, except the data of *Lin and Demore* [1973], which do not deviate significantly from other values, supporting evidence [*Steinfeld et al.*, 1987] that Φ is independent of temperature in this wavelength region. For λ<305 nm, Φ falls steadily with decreasing wavelength. A linear fit to data of *Trolier and Wiesenfeld* [1988] yields

$$\Phi(\lambda) = 1.98 - \frac{301\ \text{nm}}{\lambda} \quad \text{for } 271 < \lambda < 305\ \text{nm}. \quad (6)$$

For 222≤λ≤271 nm, Φ=0.87 within experimental uncertainty. These results are in better agreement with experiment than those of *DeMore et al.* [1992] (see Figure 2).

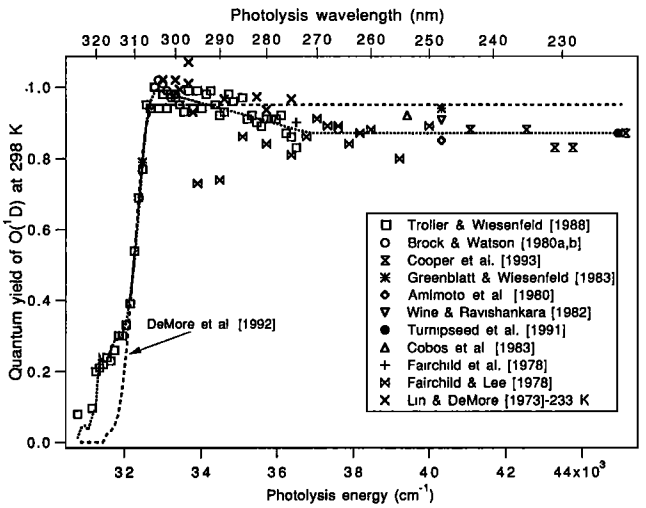

Figure 2. Φ at wavelengths 222-325 nm. The model is given by Table 1 and Eq. (5) (T=298 K) for λ≥305 nm, Eq. (6) for 271<λ<305 nm, and a constant (0.87) for 222≤λ≤271 nm. Error bars have been removed for clarity.

Atmospheric implications

Production of nitrogen oxides from the decomposition of N_2O is regulated by the concentration of O(¹D) in the stratosphere. Global amounts of OH, the primary oxidant of numerous carbon, hydrogen, nitrogen, and sulfur compounds, are controlled by reaction of O(¹D) with H_2O. Reactions involving OH and HO_2 are a major sink for O_3 in the upper and lower stratosphere [*P. O. Wennberg*, submitted, 1994].

Calculated concentrations of O(¹D) and OH for the lower stratosphere are larger by as much as 40 and 15%, respectively, compared to results from models that neglect photolysis of excited O_3, as shown in Figure 3. Effects are larger in the lower than in the upper stratosphere because at lower altitudes production of O(¹D) from photolysis of O_3 occurs at longer wavelengths. Concentrations of O(¹D) in the tropical

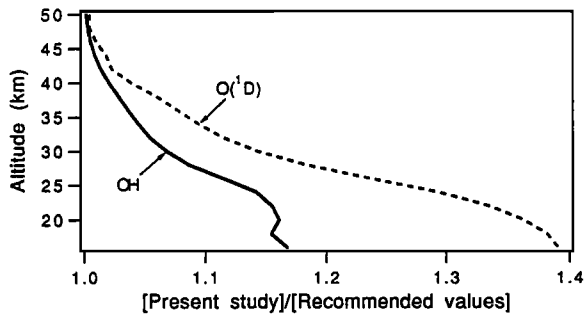

Figure 3. Comparison of calculated stratospheric concentrations. Shown for OH (solid line) and O(¹D) (dotted line) is the ratio of the 24 hour concentration or 30N at equinox, calculated using Φ given by Table 1 and Eqs. (5) and (6), relative to concentrations calculated using recommended values [*DeMore et al.*, 1992]. Results were obtained using a photochemical model constrained by data for O_3, H_2O, and CH_4 from the Atmospheric Trace Molecule Spectroscopy Experiment, for aerosol loading typical of non-volcanic conditions [*Minschwaner et al.*, 1993].

troposphere increase by 20-40%; those of OH increase by 3-14% [*D. J. Jacob*, private communication, 1994].

Conclusions

Our study suggests that photolysis of vibrationally excited O_3 is responsible for production of O(¹D) for wavelengths between 311 and 320 nm. We have developed a model that predicts the quantum yield of O(¹D) in the wavelength range 222-325 nm at temperatures relevant for atmospheric calculations, including temperatures outside the range of measurements (233-298 K). Lower stratospheric concentrations of O(¹D) and OH calculated using our model are increased by as much as 40% and 15%, respectively, compared to results from models that use recommended values for the quantum yield. The importance of O(¹D) and OH for regulating the composition of the global atmosphere underscores the need for additional laboratory measurements of the production of O(¹D) at high spectral resolution and temperatures characteristic of the lower stratosphere (~220 K).

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